IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

PARKER-HANNIFIN CORPORATION,

Plaintiff,

v.

ZIPPERTUBING (JAPAN), LTD.,

Defendant,

Civil Action No. 06-751-MPT

REDACTED

DECLARATION OF WILLIAM J. MARSDEN, JR. IN SUPPORT OF ZIPPERTUBING'S ANSWERING CLAIM CONSTRUCTION BRIEF

WILLIAM J. MARSDEN, JR. declares:

1.   I am a member of the bar of the State of Delaware and have been admitted to practice by this court. I have personal knowledge of the facts stated herein and would testify to them under oath if called upon to do so.

2.   I am an attorney in the law firm of Fish & Richardson, P.C, counsel for Defendant, Zippertubing (Japan) Ltd. ("Zippertubing") in this matter.

3.   I make this declaration to identify documents submitted with Zippertubing's Answering Claims Construction Brief.

4.   Exhibit 1 is a true and correct copy of W. Denney Freeston, Jr., Knife Coating of Porous Substrates, in Coated Fabrics Technology: A Collection of Papers from the Journal of Coated Fabrics 27 (Technomics 1971).

5.   Exhibit 2 is a true and correct copy of John C. Zemlin, Development of a 100% Solids Urethane Fabric Coating Process, Coated Fabrics Technology, Newton, MA , March 28-29,1973 (AATC 1973).
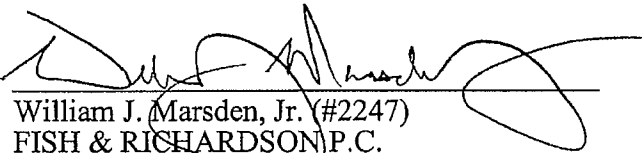
REDACTED

6.   Exhibit 3 is a true and correct copy of N.A. Favstritsky and J.-L. Wang,

Flame-Retardant Brominated Styrene-Based Polymers. X. Dibromostyrene Grafted Latexes, 69

J. Coating Tech. 39 (May 1997).

7.   Exhibit 4 is a true and correct copy of a confidential excerpt from the

Deposition of   in Parker-Hannifin v. Schlegel Electronic Materials, Inc., Civil

Action No. 1:07-cv-266-MPT.

8.   I declare under the penalty of perjury that the foregoing is true and correct.

Dated: July 15, 2008   FISH & RICHARDSON P.C.

By:
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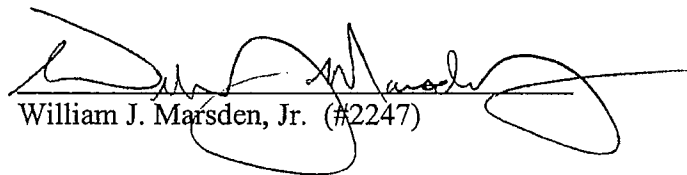*ZIPPERTUBING (JAPAN), LTD.*

CERTIFICATE OF SERVICE

I hereby certify that on July 15, 2008, I electronically filed with the Clerk of Court this **Declaration of William J. Marsden, Jr. in Support of Zippertubing's Answering Claim Construction Brief** using CM/ECF which will send electronic notification of such filing(s) to the following Delaware counsel. In addition, the document was caused to be served on the attorneys of record, at the following addresses and in the manner indicated::

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EXHIBIT 1

COATED FABRICS TECHNOLOGY

**A Collection of Papers from the
Journal of Coated Fibrous Materials**

COATED FABRICS TECHNOLOGY

A Collection of Papers from the
Journal of Coated Fibrous Materials

W. Denney Freeston, Jr.

Fabric Research Laboratories, Inc.
Dedham, Mass.

Knife Coating of Porous Substrates

ABSTRACT: A theoretical analysis of the knife coating of porous substrates is derived. The purpose of this analysis is to obtain a better understanding of the effects on the penetration of the coating material of the knife geometry, clearance between the knife and substrate, rheological properties of the coating material, coating speed, and porous nature of the substrate.

KEY WORDS: Knife coating, theory, analysis, fluid dynamics, rheology, viscosity, dynamic pressure, porosity, coating speed, penetration.

INTRODUCTION

S URFACE COATINGS are applied to porous fibrous substrates for any of a number of reasons, most of which are functional in nature, although some are purely aesthetic. Often it is desired to reduce the permeability of the structure to gases or liquids, increase durability under certain use conditions, or improve compatibility of the surface with its surroundings. A coated fabric may also be easier to care for than uncoated fabric, or it may just look nice. No matter what the reason for the coating, and no matter how it is to be applied, control of the penetration of the viscous liquid into the porous substrate is absolutely essential. Too little penetration can result in an inadequate bond; too much in excessive stiffening, reduced tearing strength, and an unacceptable appearance on the underside of the coated material. At the present time, penetration control depends largely upon skill and experience of the coating manufacturer and the coater, and the general excellence of the products attests to that skill. Nevertheless, it is unsettling to realize that we understand very little about this complicated but commercially extremely important process. It was to contribute to an improved understanding of the basic mechanics of knife coating that the work described herein was carried out.

The application of coatings to fibrous substrates is a rather complex problem in fluid dynamics. In some of its aspects, it has much in common with

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the hydrodynamic theory of lubrica-
tion to which a good deal of study has
been devoted [1]. Several examples
of the application of this theory to the
blade coating of paper exist in the
published literature, of which only
two will be mentioned. Windle and
Beazley [2] have studied the hydro-
dynamic pressure developed under

Figure 1. *Knife Coating Model*

the blade of a paper coating machine from a theoretical point of view, while
Follette and Fowells [3] have provided experimental verification of some of
these principles. The dynamic interaction of the coating and the substrate has
also been discussed by many authors. For example, penetration of viscous liq-
uids into a porous system was studied by Bøhmer and Lute [4], and Lazor
[5] has discussed the influence of the rheology of the coating paste.

These examples of published work, along with others which can be
found in the literature dealing with paper coating, represent an important
contribution to our understanding of the processes. Unfortunately, similarly
detailed studies of the fluid dynamics of coating more porous substrates
such as woven or knitted fabrics, or non-woven fibrous webs, do not exist.
These substrates and the techniques used for coating them, give rise to
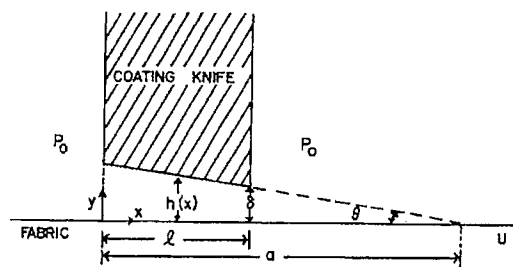considerations which differ in significant ways from those applicable to
paper processing.

MODEL

A pictorial representation of a coating knife-fabric interface is shown
in Figure 1. The knife is at rest and the fabric moves at the constant velocity
U with respect to it; the coating material flow takes place in the wedge-
shaped channel between the knife and the fabric. Since this model is anal-
ogous to the lubrication of slipper bearings, the hydrodynamic theory of
lubrication can be applied to the analysis of the knife coating of fabric.

It is recognized that not all coating knives are of the shape shown in
Figure 1. Many used in commercial coating have a square lower edge and
are held vertically, tilted forward or tilted back depending on the coating
material and the product to be produced. When the square edged blade is
tilted forward or is vertical, the fabric blade interface is of the form shown
in Figure 1; when the blade is tilted back, other considerations may be in-
troduced which would alter the analysis, and possibly the implications of its
results, from those discussed herein. A thick blade with a rounded edge
is also often used. An analysis for this blade geometry was not undertaken,
since mathematical complications did not appear warranted at this time.

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In principle, however, the approach would not be greatly different, and the results of the analysis would probably be quite similar to those obtained below for a blade with a beveled edge, since the critical region of the knife-fabric interface would be essentially the same as that shown in Figure 1.

It is assumed that the distance $h(x)$ between the knife and the fabric is very small compared to the thickness l of the knife. Also, the fabric is approximated initially by a plane, nonporous surface. Since in reality the surface of a fabric is rough and the coating penetrates the fabric, $h(x)$ represents the distance from the knife to the surface of the fabric plus some fraction of the fabric thickness.

DYNAMIC PRESSURE UNDER THE COATING KNIFE

A complete description of the motion of a compressible fluid requires not only the fundamental equations of fluid motion (i.e., the Navier-Stokes equations) [1], but also the equation of state which gives the relationship between pressure, density and temperature in the fluid, and the energy equation which specifies a balance between heat and mechanical work. However, since the knife is assumed stationary and the fabric moving with constant velocity U, the knife coating of a fabric can be considered a steady-state process. Additionally, the coating material can be treated as an incompressible fluid ($\rho =$ constant). Temperature variations in the fluid can be assumed small although this temperature may be different from that of the surroundings. Also, since the shearing rate can be assumed constant, the viscosity also may be assumed constant. (However, the appropriate value for the fluid temperature and the shearing rate is still required.) Therefore the equation of state and the energy equation become superfluous in calculations of the flow field.

Furthermore, since fabric coating can be treated as a steady-state process, all terms in the Navier-Stokes equations containing derivatives with respect to time can be equated to zero. Because the coating knife is also assumed very long and the fabric wide, the problem involves only two dimensions. Letting x, y, z denote the three orthogonal directions of the Cartesian coordinate system and u, v, w the three respective orthogonal components of the velocity vector, all terms containing derivatives with respect to z can be equated to zero and $w = 0$.

With the foregoing simplifications the equations of motion reduce to

$$\rho \left(u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = -\frac{\partial p}{\partial x} + \mu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)$$

$$\rho \left(u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) = -\frac{\partial p}{\partial y} + \mu \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right)$$

$$(1)$$

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where ρ is the fluid density, μ the viscosity and p denotes the difference between the total pressure and the hydrostatic pressure (pressure at rest). This definition of p results in cancellation of the body forces since they are in equilibrium with the hydrostatic pressure.

It is further assumed that although the convective acceleration $u\dfrac{\partial u}{\partial x}$ is different from zero, the viscous forces are considerably greater than the inertia forces and thus the inertia terms can be omitted from the equations of motion. An estimate of the ratio of the inertia forces to the viscous forces is

$$\frac{\text{Inertia Forces}}{\text{Viscous Forces}} = \frac{\rho u\, \partial u/dx}{\mu\, \partial^2 u/\partial y^2} = \frac{\rho U^2/l}{\mu\, U/h^2} = \frac{\rho U h^2}{\mu l} \qquad (2)$$

Since the inertia forces are proportional to the square of the velocity whereas the viscous forces are proportional to the first power of the velocity, a flow for which inertia forces are neglected is obtained when the velocity and thus Reynolds number is very small. When the inertia terms are omitted from the equations of motion, the resulting solutions are approximately valid for $Re \ll 1$. The reduced Reynolds number is given by [1]

$$Re^* = \frac{\rho\, Ul}{\mu}\left(\frac{h}{l}\right)^2 \qquad (3)$$

The following are typical ranges of values for the parameters in the reduced Reynolds number for laboratory and commercial knife coating of fabric:

U = 4 to 10 yards/minute (commercial)
        4 to 10 feet/minute (laboratory)
μ = 10,000 to 80,000 centipoises
ρ = 1 to 1.5 gms/cm^3
δ = 0 to 10 mils
θ = 30° (typical)
l = 0.125 to 0.250 inch

Therefore, using h at $x = l/2$,

$$0 < Re^* < 0.03.$$

Thus for all practical cases $Re^* \ll 1$ when knife coating fabric.

The second of Equations (1), the equation for the y direction, can be omitted altogether because the component v of the coating material flow velocity is very small with respect to u. The pressure gradient in the y direction is also small and can be neglected. In the equation for the x direction $\dfrac{\partial^2 u}{\partial x^2}$ can be neglected with respect to $\dfrac{\partial^2 u}{\partial y^2}$ because the former is smaller

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than the latter by a factor of the order $(h/l)^2$. With these simplifications, the differential Equations (1) reduce to

$$\frac{dp}{dx} = \mu \frac{\partial^2 u}{\partial y^2} \tag{4}$$

and the equation of continuity in differential form can be replaced by the condition that the volume rate of flow in every vertical plane under the knife must be constant:

$$Q = \int_0^{h(x)} u \, dy = \text{const.} \tag{5}$$

The boundary conditions are:

$$y = 0 : u = U; \quad x = 0 : p = p_0$$
$$y = h : u = 0; \quad x = l : p = p_0 \tag{6}$$

i.e., the pressure distribution must satisfy the condition that $p = p_0$ on both sides of the knife.

The solution of Equation (4) which satisfies the boundary conditions is

$$u = U\left(1 - \frac{y}{h}\right) - \frac{h^2 \left(\dfrac{dp}{dx}\right)}{2\mu} \frac{y}{h}\left(1 - \frac{y}{h}\right) \tag{7}$$

where the pressure gradient dp/dx must be determined in such a way as to satisfy the continuity Equation (5) and the boundary conditions for pressure. Inserting (7) into (5)

$$Q = \frac{Uh}{2} - \frac{h^3}{12\mu}\left(\frac{dp}{dx}\right) \tag{8}$$

or, solving for dp/dx

$$\frac{dp}{dx} = 12\mu\left(\frac{U}{2h^2} - \frac{Q}{h^3}\right) \tag{9}$$

Hence, by integration

$$p(x) = p_0 + 6\mu U \int_0^x \frac{dx}{h^2} - 12\mu Q \int_0^x \frac{dx}{h^3} \tag{10}$$

Inserting the condition $p = p_0$ at $x = l$

$$Q = \frac{1}{2} U \frac{\displaystyle\int_0^l \frac{dx}{h^2}}{\displaystyle\int_0^l \frac{dx}{h^3}} \tag{11}$$

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Thus the mass flow is known when the shape of the flow channel is given as the function $h(x)$. Equation (9) gives the pressure gradient, and Equation (10) gives the pressure distribution over the knife edge.

In the case of a knife with a flat face for which $h(x) = \tan\theta(a\text{-}x) \cong \theta(a\text{-}x)$ (assuming $\theta < 30°$) where a and δ are constants (see Figure 1)

$$Q = U\,\frac{\theta(a-l)a}{2a-l} \tag{12}$$

and for the pressure distribution

$$p(x) = p_0 + 6\mu\,U\,\frac{x(l-x)}{h^2(2a-l)}. \tag{13}$$

The pressure $p_{\textstyle\dagger}$ at the center of the knife, $x = l/2$, is given by

$$p_{\textstyle\dagger} = p_0 + \frac{3}{2}\,\mu\,U\,\frac{l^2}{h_m^2(2a-l)} \tag{14}$$

where $h_m = h$ at $x = l/2$, i.e., the distance between the knife and the fabric at the midplane of the knife. For small angles of inclination between the knife and the fabric the pressure distribution from Equation (13) is nearly parabolic. Hence the mean pressure difference becomes:

$$p_m = \mu U\,\frac{l^2}{(2a-l)h_m^2} \tag{15}$$

From Figure 1

$$h_m = \delta + \frac{l}{2}\tan\theta \cong \delta + \frac{l}{2}\,\theta \tag{16}$$

and

$$a = \frac{\delta + l\tan\theta}{\tan\theta} \cong \frac{\delta + l\theta}{\theta} \tag{17}$$

Therefore Equation (15) can be rewritten in the following form

$$p_m = \frac{\mu\,U\,l^2\theta}{2\left(\delta + \dfrac{l}{2}\,\theta\right)^3} \tag{18}$$

For cases where $\delta << h_m$, Equation (18) can be further simplified

$$p_m = \frac{4\mu\,U}{l\theta^2} \tag{19}$$

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As this expression shows, the greater the viscosity μ of the coating material, the faster the fabric is moving, the thinner the knife and the smaller the angle θ, the greater is the mean pressure generated under the knife. Of these four variables, the one that has the greatest effect on the pressure and the one that can be most readily varied is the angle θ of the blade to the fabric. Fabrics are usually coated at the fastest possible speeds because of economic considerations. The thickness of the knife is dictated by structural considerations. The viscosity of the coating material is a complex variable whose influence can be varied within several orders of magnitude. However, as discussed below, this influence is neither simple nor usually predictable.

The foregoing analysis also indicates that the angle of the sides of the coating knife with the fabric surface should have only a small secondary effect on the pressure generated under the knife edge. Additionally, since very high pressures are generated under the knife, the height of the reservoir of coating material behind the knife does not have a significant effect on the pressure.

COATING VISCOSITY

Coating materials rarely have simple, Newtonian viscosity characteristics. Usually they display some degree of thixotropy or pseudoplasticity, and occasionally they are dilatant [5]. This means that their viscosity is dependent on shear rate and time. It is also strongly temperature dependent. The general magnitude of the viscosity can be altered by means of additives, but at the same time these are likely to alter the thixotropy of the system. Thus, while one can vary the viscosity under the knife, and therefore the value pertinent to Equation (19) this cannot be done without regard to the effect on the viscosity at other shear rates or temperatures which may be encountered after the spreading operation.

For the remainder of this discussion, which deals with penetration of the coating into pores, it will be assumed that the viscosity is μ', which is different from μ in Equation (19). In an actual case, a pore size distribution will imply a range of shear rates, and therefore a viscosity distribution as well, so assigning a single value for the viscosity is an over-simplified representation of reality. Nevertheless, it will serve as a good approximation to indicate the effect of coating rheology, with the realization that the derived expressions cannot be applied quantitatively without dealing more precisely with the rheological problems.

PENETRATION INTO A POROUS SUBSTRATE

The actual penetration of the coating material under the knife into the substrate being coated can be treated as viscous flow through an aggregation

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of very small channels. The channels in a woven or nonwoven fibrous struc-
ture are similar in shape and arrangement to the spaces within a bundle
of randomly oriented short cylinders. As the fluid penetrates the structure
it will flow successively through channels of varying size. A stream flowing
through a large pore space will be divided into several streams which flow
through smaller spaces and then unite with each other or with other streams
at the next large pore space, etc.

In a dense woven or nonwoven structure the coating material flows be-
tween fibers and consequently all the channels are relatively small in cross-
section. However, when coating a moderately open woven structure, in
addition to penetration of the coating material between fibers, it flows be-
tween the yarns. For most structures these latter channels are substantially
larger than the channels between the fibers in the yarns. However, the cross-
sectional area of the channels between the yarns also varies along the chan-
nel length. Consequently the channels in a fibrous structure can be visual-
ized as sets of short capillaries connected in series with the cross-sectional
area of the capillaries in each set varying along their length.

An exact analysis of such a structure appears sufficiently complex to
question the wisdom of attempting it for the knife coating of fabric. Instead,
the following simplified model of channels in a fibrous structure is used. An
aggregation of parallel capillaries, circular in cross-section, going from one
fabric surface to the other is assumed [6]. Each capillary consists of numer-
ous uniform capillaries (capillaries with a constant cross-sectional area)
having various lengths and cross-sectional areas connected in series. In this
model each capillary of varying cross-sectional area in the fibrous structure
is replaced by a uniform capillary having the same resistance to viscous flow.
Similarly, each group of capillaries that feed or are fed by larger capillaries
are replaced by single capillaries having the same resistance to viscous flow.

The fraction of the total number n of capillaries per unit volume of the
fibrous structure having the radius r and length l is denoted herein by the
function $\Phi(r,l)$ where

$$\Phi(r,l) = \frac{N(r,l)}{\Delta r \Delta l \Sigma N(r,l)} \qquad (20a)$$

Δr is a small increment of capillary radius, Δl is a small increment of capillary
length, $N(r,l)$ is the total number of capillaries per unit volume which have
a radius within $\pm \Delta r/2$ of any prescribed radius r $(0 < r < \infty)$ and length
within $\pm \Delta l/2$ of any prescribed length $l(0 < l < \infty)$, and $\Sigma N(r,l) = N_T$
is the sum of all such total numbers of capillaries. In the limit, i.e., as Δr and
Δl both approach zero, Equation (20a) can be used to define $\Phi(r,l)$ as a
continuous function:

$$\Phi(r,l) = \frac{1}{N_T} \frac{d^2N}{dr\,dl} \qquad (20b)$$

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From this definition of the distribution function $\Phi(r,l)$

$$\sum_{k=1}^{n} \Phi(r_k^*, l_k^*) \, \Delta r_k \, \Delta l_k = \sum_{k=1}^{n} \frac{N(r_k^*, l_k^*)}{\Delta r_k \, \Delta l_k \, N_T} \, \Delta r_k \, \Delta l_k = 1 \qquad (21)$$

where

$$r_k \leq r_k^* \leq r_{k+1}, \, 0 \leq r_k \leq \infty, \, l_k \leq l_k^* \leq l_{k+1}, \, 0 \leq l_k \leq \infty.$$

If the function $\Phi(r,l)$ is continuous throughout the range of values of r and l, increments of length Δr_k and Δl_k approach zero and the number of increments n approach infinity, the above relation can be expressed as an integral

$$\lim_{\substack{\Delta r \to 0 \\ \Delta l \to 0}} \sum_{k=1}^{\infty} \Phi(r_k^*, l_k^*) \, \Delta r_k \, \Delta l_k = \int_{l=0}^{\infty} \int_{r=0}^{\infty} \Phi(r,l) \, dr \, dl \qquad (22)$$

and from Equation (20b),

$$\int_{l=0}^{\infty} \int_{r=0}^{\infty} \Phi(r,l) \, dr \, dl = \frac{1}{N_T} \int_{l=0}^{\infty} \int_{r=0}^{\infty} \frac{d^2 N}{dr \, dl} \, dr \, dl = 1 \qquad (23)$$

This conversion of the summation to the integral presumes a sufficiently large number of capillaries per unit volume of the fibrous structure to exist so that discrete capillaries can be replaced by a continuum.

The actual internal pore structure of a real material can be determined by Mercury Penetration.* In this procedure the size and quantity of the pores are measured by determining the quantity of mercury which can be forced into the material at various pressures [7]. Mercury wets few materials, thus it will not penetrate pores unless forced. Under pressure mercury will penetrate circular pores, in accordance with the expression

$$pD = -4\sigma \cos \psi \qquad (24)$$

where p is the applied pressure, D the diameter of the pore, σ the surface tension of mercury, and ψ the contact angle between mercury and the material forming the opening. Additionally the volume of the mercury forced into the pore is a direct function of the pore volume distribution. Thus, a penetrated volume-pressure curve can be converted into an effective cross section-pore number distribution curve.

The analysis of the flow through a straight tube of circular cross-section is the classical case of the Hagen-Poiseuille theory of flow through a pipe. An outline of the analysis follows [1]:

Let the x-axis be the axis of the pipe and r denote the radial coordinate

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* e.g., Mercury Penetration Porosimeter manufactured by Micromeritics Instrument Corp., Norcross, Georgia.

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measured from the axis outwards. The velocity components in the tangential and radial directions are zero; the velocity component parallel to the x-axis, denoted by u, depends on r alone, and the pressure is constant in every cross-section. Of the three Navier-Stokes equations in cylindrical coordinates, only the one for the axial direction remains, and it simplifies to

$$\mu' \left(\frac{d^2 u}{dr^2} + \frac{1}{r} \frac{du}{dr} \right) = \frac{dp}{dx}. \tag{25}$$

The boundary condition is $u = 0$ at $r = R$, where R is the radius of the pipe. The solution of Equation (25) is

$$u(r) = \frac{-1}{4\mu'} \frac{dp}{dx} (R^2 - r^2) \tag{26}$$

where $-dp/dx = (P'_1 - P_2)/l = $ constant is the pressure gradient along the pipe or capillary. This expression is an exact solution of the Navier-Stokes equations.

The mean velocity $\overline{u}$ of the flowing fluid is

$$\overline{u} = \frac{R^2}{8\mu'} \left(\frac{-dp}{dx} \right), \tag{27}$$

the volume rate of flow is

$$Q = dV/dt = \pi R^2 \overline{u} = \pi R^4 (-dp/dx)/8\mu' \tag{28}$$

and the pressure drop through a uniform capillary of length x is

$$\Delta p = \int_0^x \frac{8\mu'}{\pi R^4} \frac{dV}{dt} dx \tag{29}$$

The laminar flow described by the foregoing expressions occurs in practice only when the Reynolds number $Re = \overline{\rho u} R / \mu'$ is less than approximately 2300. The flow becomes turbulent for values greater than 2300. However, it can be shown that the Reynolds number of the flow of coating into the fabric pores would indeed be small.

The distance x the fluid flows in a given period of time t is obtained from Equation (27) as follows

$$\overline{u} = \frac{dx}{dt} = \frac{R^2}{8\mu'} \frac{\Delta p}{x}$$

$$\int_0^x x \, dx = \int_0^t \frac{R^2 \Delta p}{8\mu'} dt \tag{30}$$

$$\therefore x = \sqrt{\frac{R^2 \Delta p \, t}{4\mu'}}$$

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Neglecting entrance effects, to a first approximation, the pressure drop through capillaries connected in series can be assumed additive. Therefore, the pressure differential from the surface of the fibrous structure into which the fluid is flowing to the depth x, per unit surface area of the structure is given by

$$\Delta p = \int_{x=0}^{x} \sum_{k=1}^{n} N(r_k, l_k) \frac{8\mu'}{\pi r_k^4} \frac{dV}{dt} dx$$

$$= \int_{x=0}^{x} \sum_{k=1}^{n} \frac{8\mu'}{\pi r^4} \frac{dV}{dt} N_T \Phi(r_k, l_k) \Delta r_k \Delta l_k dx \qquad (31)$$

If $\Delta r_k \to 0$, $\Delta l_k \to 0$ and $n \to \infty$, the above expression for the pressure drop through the fibrous structure can be expressed in integral form

$$\Delta p = \frac{8\mu'}{\pi} \frac{dV}{dt} \int_{x=0}^{x} \int_{l=0}^{\infty} \int_{r=0}^{\infty} N_T \frac{\Phi(r,l)}{r^4} dr dl\, dx \qquad (32)$$

Performing the integration with respect to x

$$\Delta p = \frac{8\mu'x}{\pi} \frac{dV}{dt} \int_{l=0}^{\infty} \int_{r=0}^{\infty} N_T \frac{\Phi(r,l)}{r^4} dr dl \qquad (33)$$

Rewriting Equation (33) the total volume rate of flow of fluid through a unit area of the fibrous structure is

$$\frac{dV}{dt} = \frac{\pi}{8} \frac{\Delta p}{x} \frac{1}{\mu'} \frac{1}{\int_{l=0}^{\infty} \int_{r=0}^{\infty} N_T \frac{\Phi(r,l)}{r^4} dr dl} \qquad (34)$$

At any distance x through the fibrous structure the rate of flow dx/dt will not be uniform; it will vary from channel to channel. However, if it is assumed that the range of cross-section dimensions along all channels is roughly similar, the variation in rate of flow among the channels will appear only as minor irregularities in the surface which marks the average distance the fluid has penetrated throughout the fibrous structure. (In general, this is what is actually observed when coating fabric.) This approximately uniform rate of flow dx/dt can be determined by equating the volume rate of flow corresponding to a uniform rate in every channel, i.e.,

$$\frac{dV}{dt} = \frac{dx}{dt} \int_{l=0}^{\infty} \int_{r=0}^{\infty} \pi r^2 N_T \Phi(r,l) dr dl \qquad (35)$$

to that given by Equation (34).

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$$\frac{dx}{dt} = \frac{1}{8\mu'} \frac{\Delta p/x}{\left[\int_{l=0}^{\infty} \int_{r=0}^{\infty} r^2 N_T \Phi(r,l) \, dr dl \right] \left[\int_{l=0}^{\infty} \int_{r=0}^{\infty} N_T \frac{\Phi(r,l)}{r^4} \, dr dl \right]} \quad (36)$$

Separating variables and integrating the left hand side of Equation (36) with respect to x and the right hand with respect to time, the following expression is obtained for the distance the fluid penetrates the fibrous structure as a function of time, pressure differential, fluid viscosity, the total number of capillaries per unit volume and the capillary dimensions.

$$x = \sqrt{\frac{\Delta p \, t}{4\mu' \left[\int_{l=0}^{\infty} \int_{r=0}^{\infty} r^2 N_T \Phi(r,l) \, dr dl \right] \left[\int_{l=0}^{\infty} \int_{r=0}^{\infty} N_T \frac{\Phi(r,l)}{r^4} \, dr dl \right]}}$$

$$(37)$$

This expression is identical in form to Equation (30) and reduces to Equation (30) for the case of flow through a single uniform capillary of radius R.

For knife coating of fabric, the degree of penetration of the coating material into the fabric is given by Equation (37) with the Δp replaced by the pressure generated under the knife, Equation (19). Carrying out this substitution and noting that t is the length of time the fabric is under the knife, and therefore $l/t = U$, the running speed of the fabric, the following expression is obtained.

$$x = \sqrt{\frac{\mu/\mu'}{\theta^2 \left[\int_{l=0}^{\infty} \int_{r=0}^{\infty} r^2 N_T \Phi(r,l) \, dr dl \right] \left[\int_{l=0}^{\infty} \int_{r=0}^{\infty} N_T \frac{\Phi(r,l)}{r^4} \, dr dl \right]}} \quad (38)$$

This equation indicates that the degree of penetration of the coating material is independent of the speed of the fabric, thereby verifying the validity of extrapolating the results of investigations on laboratory coaters to high-speed production machines.

Equation (38) also shows that for a given fabric the variable that has the largest effect on the degree of penetration of coating material achieved in knife coating is the angle θ the blade makes with the surface of the fibrous structure. The smaller the angle, the greater the penetration due to the increased pressure generated under the knife.

The presence of the viscosity ratio $\left(\dfrac{\text{viscosity under the knife}}{\text{viscosity in the pores}} \right)$ in the numerator of Equation (38) indicates that the penetration is dependent upon the shearing rate dependency of the viscosity, and not upon its absolute

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Knife Coating of Porous Substrates

level. Clearly some minimum viscosity limit must be imposed upon this statement, since the assumption that the pressure generated under the knife was significantly greater than that due to the action of any other external force such as gravity was implicit in the derivation. This condition is met by most normal coating materials. Thus, it is in general a valid and most significant observation that it is the pseudo-plasticity of the coating material which plays an important role in determining the degree of penetration, and not the absolute value of the viscosity at any given shearing rate.

TYPICAL SHEARING RATES

Newton's law of friction says

$$\tau = \mu \frac{du}{dy} \tag{39}$$

where τ denotes shear stress and the other terms are as previously defined. From the analogy between this law and Hooke's law for an elastic solid body, the velocity gradient du/dy can be thought of as the rate of change of the shear strain (or shearing rate) in the fluid.

The shearing rate under the coating blade is given by the first differential of Equation (7) with respect to y. Carrying out this operation and substituting Equation (9)

$$\frac{du}{dy} = -\frac{U}{h} - \left(\frac{U}{2h^2} - \frac{Q}{h^3} \right) (6h - 12y) \tag{40}$$

where Q is given by Equation (12). This expression shows that the shearing rate is a maximum at the fabric surface and decreases with increasing distance from the fabric.

Similarly, the shearing rate in the fabric pores is given by the first differential of Equation (26) with respect to r

$$\frac{du}{dr} = \frac{1}{2\mu'} \frac{\Delta p}{x} r \tag{41}$$

where Δp is given by Equation (18), since the pressure at the entrance to the pores is the same as that under the knife and the pressure at the exit, i.e., the back side of the fabric, atmospheric. Equation (41) shows that the shearing rate in the pores is zero at the center and a maximum at the wall.

Using the values for U, δ, θ and l given previously and letting x equal a fabric thickness of 0.007 inch (typical value) and the pore radius $R = 0.002$-0.004 inch, i.e., the distance between yarns in typical fabrics, it can be shown that the shearing rate under the knife is two to three orders of magnitude greater than in the fabric pores.

W. D. Freeston, Jr.

CONCLUSIONS

This analysis of the fluid dynamics of knife coating of porous substrates was based on an idealized geometric model of the knife-coating-substrate interface, and on several simplifying assumptions with respect to the fluid properties of the coating material and the nature of the flow. Thus, the results would not be expected to quantitatively predict coating behavior; this must be left for future refinements both in the analysis and in our understanding of the process itself. It is not too much to hope, however, that the results can at least provide significant qualitative insights into the effect of the critical parameters of a knife coating operation. These can be summarized as follows:

(a) The dynamic pressure which develops in the fluid coating between the knife and the substrate increases with increasing coating viscosity, increasing velocity of the substrate relative to the knife, decreasing knife thickness and, most importantly, decreasing angle between the bottom surface of the knife and the surface of the substrate.

(b) This pressure plays a major role in forcing the coating into the pores of the substrate. The depth of penetration is independent of substrate velocity but increases with increasing ratio of coating viscosity at the shear rates existing under the knife to the coating viscosity at the shear rates within the pores of the substrate, that is, with the degree of coating pseudo-plasticity. It also increases as the angle between the blade and the substrate surfaces decreases and as the distribution of pore sizes in the substrate tends towards shorter and/or larger diameter pores.

These conclusions, particularly that relating penetration to the shear rate dependency of coating viscosity, explain some of the perplexing observations which have been made in the course of coating trials, and for which no satisfactory explanation could hitherto be given. The scope of usefulness of such a simplified analysis in a practical sense, however, can only be determined by relating the trends from carefully controlled experiments to those indicated by the analysis. There is little doubt that other considerations will have to be introduced before predictable control over a knife coating operation can be achieved. Limiting values of knife thickness, coating viscosity and substrate velocity must be considered. The importance of capillary effects and their relation to the surface energies of substrate and coating over the range of temperatures which will be experienced must be analyzed. And, of course, the analysis should be extended to cover other coating techniques, such as roller coating, calender coating, and transfer coating. In spite of the fact that the analysis has been so limited, the value of such an approach is clearly indicated. It is hoped that future opportunities will arise to extend and refine the work, in order to provide a sound theoretical basis

for modifying coating procedures to obtain better productivity and improved products.

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EXHIBIT 2

COATED FABRICS TECHNOLOGY

Sponsored by the

COATED FABRICS TECHNOLOGY COMMITTEE

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AMERICAN ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS

March 28-29, 1973

at the

Marriott Motor Inn

Newton, Mass.

PAPERS

Published in JOURNAL OF COATED FABRICS. Vol. 3, no. 1, July 1973, p. 31-37.

DEVELOPMENT OF A 100% SOLIDS
URETHANE FABRIC COATING PROCESS

by

John C. Zemlin

BACKGROUND

Fabric coating today is a very large and very diverse industry and a brief description of it may be helpful in delineating those areas where our process may find application. It has been estimated by one market researcher that in 1972, 60 million square yards of urethane coated fabric were produced in this country. Approximately one quarter of this production was "direct coated" fabric while three quarters were prepared by the so-called "transfer" technique. A more complete breakdown is shown in Table I.

Essentially all of the urethane coating today is done with solvent solutions of coating resins. Most of the urethane coating resins used in this country are high molecular weight, fully reacted, thermoplastic urethanes. Some use, however, is still being made of the two-part urethanes which were the basis of the first "wet look" coated fabrics of a few years ago.

In direct coating, the resin solution, a viscous liquid, is applied by knifing directly to the fabric; usually a floating knife, a knife over blanket or a knife over roll-coating technique is used. These coating techniques are illustrated in Figure 1.

ESTIMATED OUTPUT OF POLYURETHANE COATED FABRIC - 1972 *

	54" YDS. MILLIONS OF YDS.	EST. COATING WEIGHT-OZ/YD	EST. COATING THICKNESS-MILS
DIRECT COATING - TOTAL	16	2	1.5
TRANSFER COATING - TOTAL	44	2	1.5
APPAREL	22	1.5	1.0
BOOTS	6	2.0	1.5
SHOE UPPERS	3	3.0	2.0
HANDBAGS	7	1.5	1.0
UPHOLSTERY	6	5.0	3.5

* These figures are calculated from original data supplied by The Marketing/Management Services Division of The National Credit Office, New York, New York

Table I

a - Floating knife
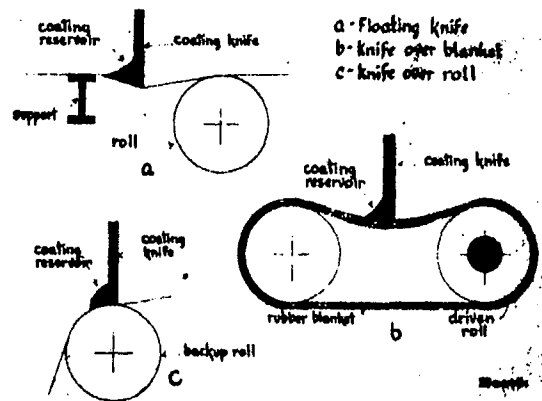b - knife over blanket
c - knife over roll

Figure 1

Usually several light coatings, followed by passage each time through a drying oven, are applied in sequence. This is necessary to prevent excessive strike through which would produce a very "boardy" hand in the fabric and also to permit complete solvent evaporation from each layer before the next is applied.

Depending on the thickness of coating needed, four, six, ten and even more individual applications are used to build up to the final desired coating thickness. Oven temperatures are limited to those where boiling and bubbling in the coating will not occur. Most frequently, solvents such as DMF, tetrahydrofuran, methyl ethyl ketone and the like are necessary to obtain reasonable resin concentrations in the coating solution.

BOSTIK 100% SOLIDS URETHANE COATING PROCESS

ADVANTAGES
- Single Coat Operation
  Uses Present Coating Heads and Ovens
- No Solvent Use
- No Heated Air Loss
  Surface Effects Possible (runner costing only)

DISADVANTAGES
- Lowest Coating Thickness 2½ mils
- Requires 2-Part Urethane Dispenser

Table II

The major disadvantage of our coating process is the requirement for minimum coating thickness. This makes it essentially impossible to prepare the very lightly coating nylon fabrics used for many athletic outerwear garments and also for lightweight tenting and tarpaulins. A problem also exists in transfer coating in duplicating leather grains with deep profiles. Alligator skin is a typical example. In this instance, the contours of the pattern paper vary by 4 or 5 mils, and since the applied coating must be about 2 mils thicker than the highest contour, a very heavy coating results.

PROCESS DESIGN CONSIDERATIONS

The use of a solvent-free liquid urethane in fabric coating both limits the type of equipment and necessitates rather precise control of several physical and chemical characteristics of the liquid system.

Almost all solvent-free urethane systems have high viscosities, measuring in the thousands of centipoises. Viscosities such as these, combined with a curing mix of limited "open time" preclude almost all coating techniques except knife coating, extrusion coating and variations of these. Our work has been essentially limited to knife coating using equipment as indicated in Figure 2.

A second restriction we have placed on our process is the need for operation at room temperature. Many urethane systems are based on materials which crystallize or congeal at room temperature. Although it is possible to provide heating to the coating section of a coating line, the resulting complications such as difficulty of access to the knife, and shortened "open time" seemed sufficiently troublesome to cause us to avoid them by using systems which are liquid at ambient temperatures.

As we proceeded in our development we found a number of practical problems which had to be met. These include, as we proceed from the first application of mixed material to the "web" or "substrate"; ready mixing in the bank before the knife, easy knifing and freedom from strike through or from drawing back into droplets (direct coating and transfer coating respectively). These problems will be considered in some detail in the following.

Since many of the above problems relate to viscosity of the mixed urethane system, let us first examine the viscosity of one system which has proven to be useful in our process. The viscosity of this material, which we call System A, has been determined on a Haake Rotovisco, RV 3 using their PK Viscosity Sensors.* The PK units are plate and cone sensors, the cone having an angle of 0.3°. The spring loaded plate fits closely into a massive metal block which is jacketed for heating and cooling. The unit is of particular advantage in that only about 0.1 gms of mixed urethane is needed for a viscosity determination - thus avoiding exotherm problems which make viscosity determinations difficult with most other viscosimeters.

The data obtained is shown in Figure 3 and indicates the viscosity as measured at 20°C. at several shear rates as the mixed material ages and gradually gels. It is quite

*Brabender International, P.O. Box 128, Rochelle Park, N.J. 07662

Transfer coating requires similar equipment to that needed for direct coatin
Transfer coating differs in that the coating is applied to a pre-patterned or emb.
release paper. Since the "strike through" is not a problem, heavier coatings can be
applied to the paper, although again the amount of coating is limited by the necessity
of obtaining complete release of solvent before recoating. And the thicker the coating,
the slower the solvent release. With light-weight goods for the apparel market, typi-
cally a heavy coating is applied to the release paper such that a dry thickness of 1 mil
is obtained. After passing the release paper through the drying oven, it is returned to
the coating head and a second coating is applied. This is an adhesive coating which may
or may not have the same composition as the first coating. Before substantial drying
occurs, the fabric is "nipped" into the adhesive layer. The combination of release paper,
coating and fabric then passes through the heating tunnel again, and at the end, the
fabric with the coating adhering to it is rolled up separately from the release paper.

Thin coatings of 1 1/2 mils may readily be applied by this process. As the coating
thickness goes up, however, so does the difficulty in carrying out the transfer coating
operation. Multiple coats must be applied and considerable care given to complete sol-
vent removal.

There are additional problems associated with present techniques for direct and
transfer coating and among them are the high cost of the solvents used, the hazards asso-
ciated with the solvent use, and the enormous amount of heated air needed to safely
exhaust the solvents. For example, a single coating line can easily consume 3,000 lbs. of
solvent in eight hours of operation.

The existence of these problems, in the coating industry, was recognized some time
ago by USM Corporation's BOSTIK DIVISION and we were asked to develop a fabric coating
process which would obviate them.

DESCRIPTION OF PROCESS

The following is a summary of part of our work, in response to the above request, on
a fabric coating process which uses solvent-free, two-part liquid urethane systems. The
process has been carried through the pilot scale of development using equipment as dia-
gramed in Figure 2. The advantages and disadvantages of the process as compared to the
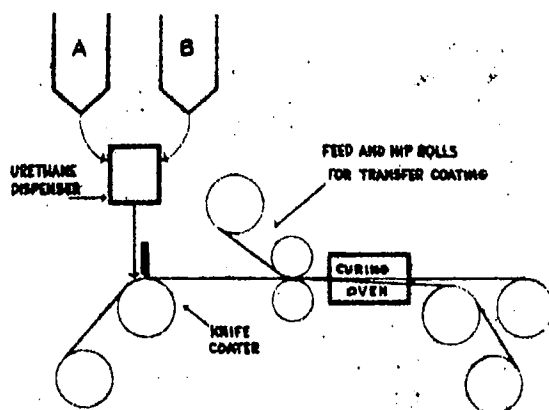present solvent coating technique can be summarized approximately as in Table II.

Figure 2

In almost all cases our process can pro-
vide the desired coating in a single coating
operation. The only exceptions would be in
instances where a coating is required on both
sides of the fabric or where a top coating is
required having different properties, say
higher hardness or different color, than those
of the bottom coating.

In general, most of the present urethane
coating lines for fabric can be utilized for
our coating operation with the addition of a
urethane dispenser. Since no solvent is used,
the very large amounts of heated air which
were formerly vented to the atmosphere need not
be used, and only a small amount of heated air
recirculation is required to control the curing
temperature.

An additional theoretical advantage is the
possibility of obtaining novel affects as by
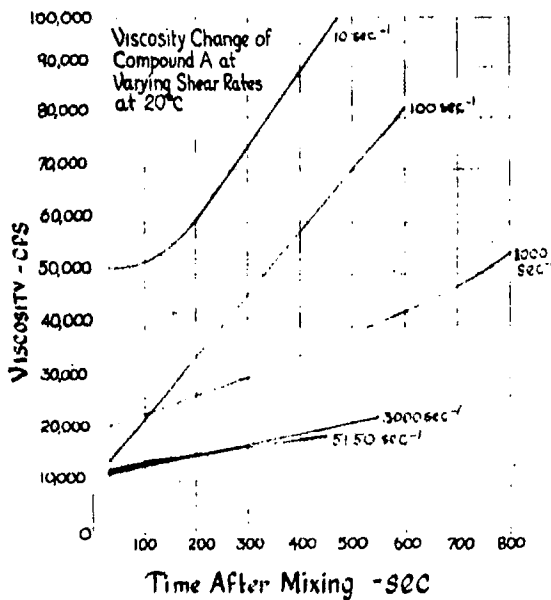the use of serated blades, air jets and the
like.

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Figure 3

obvious that the system is non-Newtonian in character. At low shear rates it has a very high viscosity which decreases sharply at higher shear rates.

During operation of our coating process, a freshly mixed material such as System A is applied to the moving web in front of the knife. The knife then permits an amount of material approximately equal to the gap between the tip of the blade and web passing below to flow on with the web. It is necessary, however, that a reservoir of material be present behind the knife in order that the knife can meter an even coating. This reservoir, called the "bank", is formed by supplying a momentary excess of material over that needed for metering. In order that the bank be maintained at a fixed size, of course, the average feed to the bank must equal the amount metered out to the web.

The steadily increasing viscosity of our systems requires that good mixing be obtained in the bank since for best operation the metering knife must have a reservoir of uniform viscosity material. Mixing does not occur unless a shear rate of reasonable magnitude exists. The shearing force in the bank is imparted by the web as the bank is restrained by the knife. A very approximate shear rate in the bank can be calculated by assuming the bank to be a cylinder rotating about a fixed center with the speed of rotation equal to the web speed and that all of the shearing force is due to the fixed knife. The equation becomes:

$$\text{Shear Rate} = \frac{\text{Difference in velocity over sheared layer}}{\text{Thickness of layer}} = \frac{\text{Web speed}}{\text{Bank radius}}$$

Although the actual situation is more complex, with highest shear rates occurring at the outside of the bank, this approximation does show patterns of change and is probably of the right order of magnitude. The calculation has been made for web speeds up to 20 yards/minute using bank diameters of 1/2", 1" and 2". The results are shown in Figure 4. Low speeds and large banks yield very low shear rates which are associated with high viscosities.
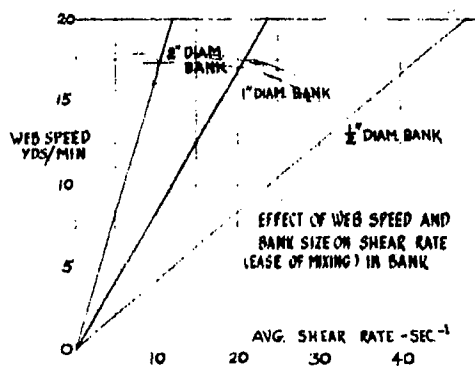
A second factor peculiar to our situation is the need to flood the bank when feeding rather than supplying uniformly thin layers equal to the metering thickness. This is necessary because fresh material has a relatively lower viscosity and if present in a thin film will tend to flow under the bank and be metered out under the knife without actually mixing into the bank. Flooding can be accomplished by the slow traversing of the mixing head or by single point deposition of mixed material.

It is important for good mixing as discussed above, and, for easy knifing, that the material in the bank be at a relatively low viscosity level.
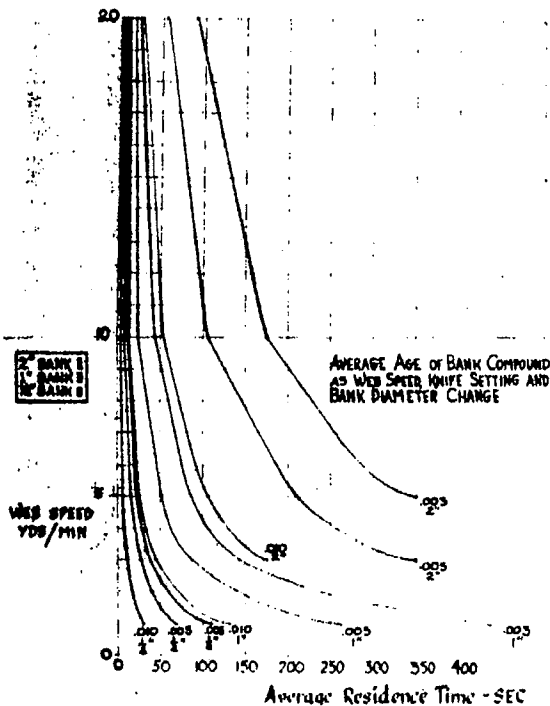

Figure 4

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Lowest viscosities are associated with freshly mixed material. A calculation of average residence time in the bank can readily be made if we assume equal input and output at the bank along with perfect mixing, i.e. no "slippage" of freshly mixed product under the bank and out under the knife. . The equation is:

Average residence time

$$= \frac{\text{Volume of bank}}{\text{Rate of adding}} \text{ new material}$$

$$= \frac{\text{Cross sectional area of bank x unit length}}{\text{Web velocity x knife opening x unit width}}$$

(As mentioned, the input of new material must be balanced by an equal loss of material under the knife if the bank is to remain at the same size.) The results of these calculations are shown in Figure 5.

The matter of bank size is thus quite important, since it affects residence time, and thus bank viscosity and because it directly affects bank shear rate or bank mixing. Further, exothermic polymerization is greatly facilitated by larger bank sizes. These factors of bank size, web speed and knife opening actually exert a "multiplier effect" and if not controlled can cause an "avalanche" type of gelling reaction in the bank. We have found with System A that a bank size of about 1 1/2" is the maximum possible at a web speed of 5 yards/minute. At slower speeds or with larger banks at this speed, mixing will not occur in center of the bank and this portion of the bank will tend to gel and solidify.

Easy knifing is also obtained if the material in the bank has a low viscosity under the high shear condition of knifing. Figure 3 shows that System A has a relatively low viscosity under shear rates of 1,000 sec.$^{-1}$ or more, and that this condition exists for an appreciable length of time after mixing. The approximate shear rate under the knife can be calculated in a manner identical to that above, i.e.

$$\text{Shear rate} = \frac{\text{Web speed}}{\text{Gap between knife and web}}$$
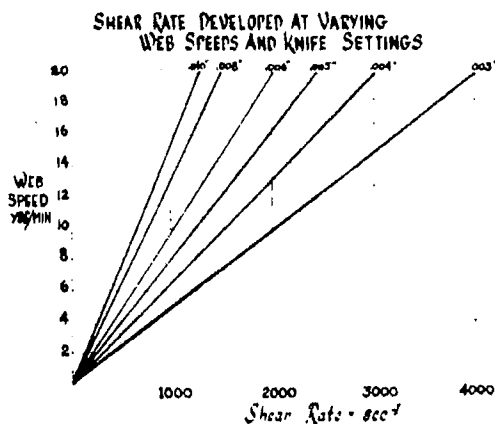
The calculated shear rates for various web speeds and knife settings are shown in Figure 6. Shear rates of the order of 1,000 sec.$^{-1}$ are obtained at higher web speeds and at smaller settings. Since commercial speeds will be at the high end of this scale most knife clearance settings will produce shear rates in the 2,000-3,000 sec.$^{-1}$ range. Thus, quite low viscosities will result during knifing.

Fabric "strike through" in coating is a function of time and viscosity at the applied shearing force for any given fabric and coating. It becomes a potential problem as soon as mixed material is deposited on the moving fabric before the knife. We have found that no appreciable strike through of our systems occurs through

Figure 5

Figure 6

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2 1/2 oz., 210 denier, plain weave, nylon fabric when the viscosity is about 20,000 cps. and the contact time is less than 30 sec. At 10,000 cps. strike through occurs in about 15 sec. Since the fabric is usually in contact with mixed material for only a fraction of a second before reaching the coating knife, initial strike through is not a problem.

Under the high shear of the coating knife, a substantial reduction in viscosity occurs. At 20°C. viscosities of about 10,000 to 15,000 cps. exist. This reduction permits easy knifing and again owing to the brief exposure to high shear conditions, strike through is rarely a problem. At higher ambient temperatures, still lower viscosities- at 40°C.,a little below 10,000 cps. with System A - are encountered as shown in Figure 7. Even, here and even on quite open fabrics, strike through does not usually become a problem with the proper knife selection.

One consideration in all fabric coating is anchorage of the coating to the fabric. Good anchorage is rarely obtained without considerable penetration into the interstices of the fabric, that is without surrounding or enveloping some of the yarns with the coating. Such penetration does not affect the flexibility or drape of the fabric to the same degree as penetration into the yarns. The novel character of our coating systems does permit penetration into the fabric interstices under high shear but without significant penetration into the yarn.

The amount of penetration into the fabric can also be controlled by the position of the knife blade above the fabric. Thus, a square edged blade set at 90° to fabric will cause only modest penetration into the fabric. If the leading edge of the blade is tapered to a 45° angle so that the blade exerts a wedging or "pumping" effect on the coating passing beneath, more penetration is obtained. In general, we have found a tapered blade of one type or another to be desirable in most types of coating, giving better coating anchorage on fabrics and better pattern reproduction on transfer coating.
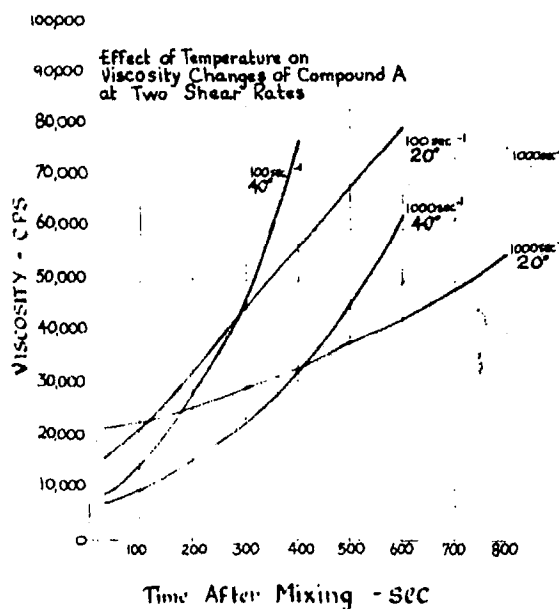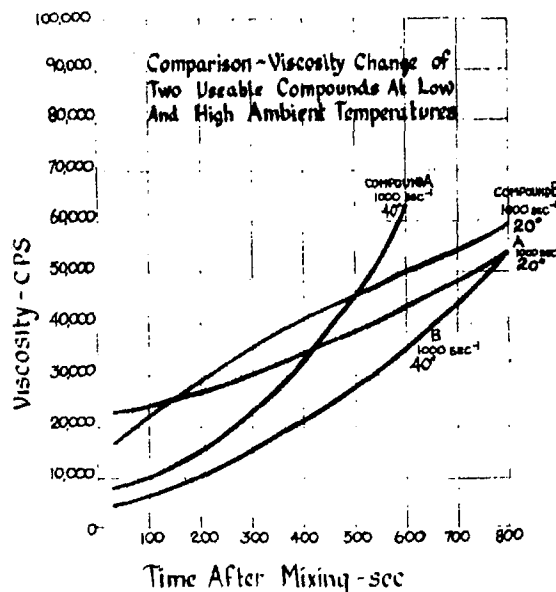

Figure 7

Figure 8

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The most trouble we encountered in our coating development was in viscosity control during heating. Curing ovens are large expensive objects and they are usually the limiting factor as far as coating line output is concerned. Since urethanes cure more rapidly at high temperatures, it is obviously desirable to have the oven at as high a temperature as practical. This method of operation means, however, that the coating applied at room temperature in a smooth thin film is suddenly exposed to hot air or to radiated heat so that its temperature rises to perhaps 100°C. in as little as 30 sec.

The difficulty is most noticeable on the silicone treated transfer paper where if any substantial reduction in viscosity occurs, the coating will tend to pinhole or draw back into droplets. Our present coatings do not decrease in viscosity to the extent that this becomes a problem.

Although only one compound, our System A, has been discussed so far, we have actually developed a series of useful compounds for our process. Extensive viscosity data has not been obtained for most of them since rapid screening for viscosity "fit" is normally all that is needed to assure their performance in our coating process. Viscosity curves comparing System A, a Shore A 55 compound with a second useful compound, a Shore A 85 material labeled System B are presented in Figure 8. The close similarity in viscosity/time behavior is evident and is typical of all of the compounds useable in our process.

This process is still considered to be in development status by USM BOSTIK DIVISION and neither samples nor chemical details of the process are available. Patent applications have been filed.

Acknowledgement

I wish to thank Robert H. Miller of USM's BOSTIK DIVISION for assistance in much of the experimental work; E. C. Stanley of Chemicals and Pigments Equipment Co., Newton, Mass. for advice and assistance in operating the Haake Rotovisco, RV-3; and R. Battersby of USM's BOSTIK DIVISION for advice in the rheological area.

EXHIBIT 3

JOURNAL OF COATINGS TECHNOLOGY

FEDERATION OF SOCIETIES FOR COATINGS TECHNOLOGY

ice

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Flame-Retardant Brominated Styrene-Based Polymers. X. Dibromostyrene Grafted Latexes

N.A. Favstritsky and J.-L. Wang—Great Lakes Chemical Corp.*

INTRODUCTION

Natural and synthetic latexes are commercially used in a variety of coatings. In many coatings applications, the latexes with flame-retarding properties are desired. This applies in particular where latexes are used in textiles, carpetings, paints, clearcoatings, adhesives, sealants, caulks, nonwoven binders, etc.

Until recently, coatings users have generally had to use flame retardants that were developed for other applications. All of these products, either liquid or solid, have had an adverse effect upon the quality of the coating. The usual method by which flame-retardant (FR) properties are imparted to latexes is the blending-in of flame retardant additives, but disadvantages, such as phase separation upon aging, plasticization and migration to the surface, coagulation and sedimentation, generation of strong white pigmenting and settling out effect, toxicity resulting from the presence of antimony trioxide, have been associated with this approach. The best solution of these problems appears to be the elimination of additive flame retardants by incorporating flame retardancy into the polymer used for coating.

We have previously reported[1-12] the synthesis of a variety of dibromostyrene (DBS) - based FR latexes. These latexes were prepared from DBS and other monomers such as (meth)acrylic acids and their esters, butadiene, vinyl acetate, and styrene. Some of the challenges have been cost, flame retardancy, coating properties, latex stability, and monomer reactivity. However, if a practical and useful FR latex can be produced by simply grafting the DBS monomers onto a commercial latex or mixture of latexes, then the cost of producing such an FR latex can be significantly reduced.

Although a vast number of grafted polymer latex compositions has been described,[13-29] none of them have been identified with polymer latex modification with bromine for flame retardance. Some of the grafted latexes are claimed to have value in improving bacteria resistance for use in paints or other coating compounds,[13] improving adhesion of the modified latex to silicate glass, aluminum foil, cellophane, and textiles,[20] increasing the

This paper describes the synthesis, characterization, and some applications of flame-retardant dibromostyrene grafted latexes. These latexes are synthesized by an emulsion polymerization technique. One of the prime factors to be considered in the choice of a commercial latex or a latex blend to be grafted is the glass transition temperature(s) of the polymer(s) in the final latex desired. The graft latexes were characterized in terms of glass transition temperature, solids content, bromine content, grafted dibromostyrene content, and flame retardancy. They are useful for a wide range of applications, including fabric backcoatings, carpetings, paints, adhesives, sealants, caulks, nonwoven binders, etc.

viscosity of the latex and its activation energy of viscous flow,[23] improving impact strength,[28,29] and latexes being useful in paper coating compositions.[27]

This paper summarizes two U.S. patents[30,31] and two papers published in the *Polymer Preprints*.[32,33] It describes the synthesis, characterization, and application of DBS graft latexes. Latexes chosen for grafting are commercial latexes, such as Rhoplex HA-24 and HA-8, Hystretch V-

Table 1—Synthesis of DBS Homopolymer (PDBS) Latex

Description	Parts
Deionized (DI) water	180
SDS	3
Potassium persulfate	0.2
DBS	100
t-DDM	0-0.2

Seal under nitrogen in 8 oz. bottle. Rotate about a horizontal axis for 2-5 hr in water bath at 50°C. Remove from water bath. Cool to room temperature

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Table 2—Synthesis of DBS Graft Commercial Latexes (Except for PB Latex)

Description	Parts	Remarks
Commercial latex	84.5-45	Dry basis
Potassium lauroate	3	Blend
DBS	15.6-55	
CHP	0.2	
TEPA	0.4	
t-DDM	0.5	
DI water	14-57.3	Dilute to final solids of 40-65%

Seal under nitrogen in 8 oz bottle. Rotate about horizontal axis for 2.4 hr in water bath at 50°C. Remove from water bath. Cool at room temperature. The results of these preparations are set forth in Table 4.

29, Airflex 465, 4500, 4514 and 4530, Pliolite SBR latex and polybutadiend (PB) latex.

The graft latexes were characterized in terms of glass transition temperature (T_g), solids content, bromine content, grafted dibromostyrene content and flame retardancy.

They are useful for a wide variety of applications, including fabric backcoatings, carpetings, paints, adhesives, sealants, caulks, non-woven binders, etc.

EXPERIMENTAL

Materials

Dibromostyrene, a product of the Great Lakes Chemical Corp., contains about 82% DBS, 12-13% monobromostyrene, and 5-6% tribromostyrene by weight. Ethyl acrylate (EA), acrylonitrile (AN), butyl acrylate (BA), styrene (S), acrylic acid (AA), and methacrylic acid (MAA) were used directly as received from Aldrich Chemical Co. Lauric acid, potassium hydroxide, sodium dodecyl sulfate (SDS), potassium persulfate, ammonium persulfate, sodium bisulfite, tetraethylenepentamine (TEPA), t-dodecyl mercaptan (t-DDM) were also used directly as received from Aldrich. Cumene hydroperoxide (CHP) from Elf Atochem and tetrahydrofuran (THF) from Baxter were used without further purification.

Characterization

Table 4 lists composition and physical properties of DBS grafted commercial latexes. The DBS graft latex was characterized in terms of T_g, solids content, bromine content, and flame retardant property. The T_g was measured by DSC at a rate of 10°C/min. Percent bromine was measured by Schöniger Combustion Method (ASTM E 442-91). This test covers the determination of chlorine, bromine, or iodine in organic compounds by the oxygen flask technique. Flame retardant property was measured by MVSS-302 flammability test when used in polyester fabric backcoatings.

The MVSS-302 test criteria, a horizontal burn test, must be met by materials used in the interior of passenger cars. A specimen 14 in. × 1/2 in. is marked at a point 1-1/2 in. from each end. One end of the specimen is ignited in accordance with test procedures, and the

amount of time it burns measured from the time flame from the burning specimen reaches the first mark. Timing is stopped at the time flaming ceased or at the time at which the flame reaches the second mark. The test calls for a burn rate (measured as the flame processes from the first mark to the second) of less than four inches per minute. A rating of self-extinguishing (SE) requires no burn beyond the first mark (1-1/2 in.). A rating of rapid burn (RB) requires that the flame travels to the second mark or a burn length of 10.0 in. that is the distance between the first and the second marks.

Table 5 lists percent DBS grafted onto commercial latexes. Percent grafting of dibromostyrene onto commercial latexes, Pliolite SBR latex, and PB latex (Goodyear Tire & Rubber Co.) was determined by THF solvent extraction: the DBS-grafted latex, 55/45-DBS/SBR or 60/40-DBS/PB, was coagulated in a 1-3% $MgSO_4$ solution under stirring. The coagulated polymer was filtered, washed thoroughly with water, and dried overnight in a vacuum oven at 50°C to a constant weight. Two grams of the dried coagulated polymer was weighed in a cellulose extraction thimble (43 mm x 125 mm) and successively extracted with THF for 48 hr.

FLAME RETARDANCE TESTING AND RESULTS

Flame Retardancy of Physical Blend vs. Graft Latex

The PDBS latex was physically blended with an ungrafted commercial latex, Rhoplex HA-24 or HA-8 to result in a latex blend containing 30 and 25% DBS, respectively. Both latex blends, coated onto an 8 oz/yd², 100% polyester fabric at a weight of 1.4-1.6 oz/yd², failed the Motor Vehicle Safety Standard (MVSS) 302 flammability test [49 CFR Ch. V. (10-1-95 Edition)] (rapid burn (RB), worst rating). At a comparable DBS level, both DBS-grafted Rhoplex HA-24 and HA-8 passed the MVSS-302 flammability test at this add-on weight (self-extinguishing (SE), best rating).

Textile Backcoating A

The 70/30-Rhopex HA-24/DBS graft latex was coated onto an 8 oz/yd² 100% polyester fabric at a weight of 1.6 oz/yd², after oven drying at 100°C for 30 min. The coating was clear and slightly firmer than the commercial latex, which is considered satisfactory. The coated fabric passed MVSS-302 flammability test with an SE (best

Table 3—Synthesis of DBS Graft PB Latex

Description	Parts	Remarks
PB latex	40	Dry basis
SDS	1	
Potassium persulfate	0.2	
Sodium bisulfite	0.2	
DI water	20	
DBS	60	
t-DDM	0.5	

Seal under nitrogen in 8 oz bottle. Rotate about horizontal axis for 6.5 hr in water bath at 50°C. Remove from water bath. Cool to room temperature. The final latex has 57.9% solids (97.6% conversion). -79°C T_g and 34.34% Br (Table 4).

Table 4—Composition and Physical Properties of Grafting of DBS onto Commercial Latexes

Example	Commercial Latex[a]	T_g, °C Comm. Latex Reported Value	T_g, °C Comm. Latex Observed	T_g, °C Graft Latex Observed	DBS Charged[b] wt%	Solids %	Br %	MVSS-302 Rating[c]
1	Rhoplex HA-24	−7	−17.2	−16.7	30.0	40-65	17.17	SE
2	Rhoplex HA-8	−10	−17.3	−15.0	25.0	40-60	14.31	SE
3	Hystretch V-29	−29	−37.6	−35.3	40.0	40-50	22.89	SE
4	Airflex 465	−5±3	----	—	25.0	40-50	14.21	SE
5	Airflex 4500	3	—	—	20.0	40-50	11.36	SE
6	Airflex 4514	12	—	—	20.0	40-50	11.45	SE
7	Airflex 4530	29	—	—	15.6	40-50	8.93	SE
8	Pliolite SBR latex	−55	−56.0	−55.2	55.0	50-60	31.35	SE
9	Polybutadiene latex	−80	−79.5	−78.9	60.0	50-60	34.34	SE

(a) Rhoplex HA-24 & HA-8 from Rohm & Haas Co.; Hystretch V-29 from BFGoodrich Co.; Airflex 465, 4500, 4514, and 4530 from Air Products and Chemicals, Inc.; Pliolite SBR and polybutadiene latex from Goodyear Tire & Rubber Co.
(b) Weight % DBS based on 100% total solids.
(c) Motor Vehicle Safety Standard (MVSS) 302 flammability test; SE = self-extinguishing.

rating) and a burn distance of 0.8 in. The same fabric backcoated with 1.6 oz/yd² of the commercial latex (Rhoplex HA-24) failed the MVSS-302 test with a burn distance of 10.0 in. (RB).

Textile Backcoating B

When 1.4 oz/yd² of 70/30-Rhoplex HA-8/DBS graft latex was coated onto the 8 oz/yd² fabric, an SE rating was obtained with a 1.4 in. burn length. The commercial latex without modification (Rhoplex HA-8) failed to pass the MVSS-302 test at this add-on weight and yielded a burn distance of 10.0 in. (RB).

Textile Backcoating C

When coated onto an 8 oz/yd², 100% polyester fabric, Hystretch V-29 latex at 3.7 oz/yd² yielded a failure in the MVSS-302 test (10.0 in. burned). The 60/10/30-Hystretch V-29/S/DBS graft latex produced a 1.6 in. burn length at 3.7 oz/yd². The graft latex had good flexibility and yet was slightly firmer than the latex ungrafted.

Contact Adhesive

The 80/20-Rhoplex HA-24/DBS graft latex was coated onto 0.5 mil Mylar polyester film. After drying 90 sec at 158°F, two pieces of film were pressed together and rolled to eliminate any bubbles. For comparison the same procedure was followed using the commercial latex (Rhoplex HA-24). Upon cooling, the films were pulled apart by hand. No significant difference in adhesion between two samples was noticed and the adhesion was judged to be adequate. Flammability was tested by wrapping the film composite loosely about a four-inch diameter cylinder of fiberglass batt insulation. A three-inch blue methane Bunsen burner flame was placed against the lower and side surfaces of the batt/Mylar construction which had been positioned at a 45°C angle from vertical. There was no observable after flame when the burner flame was removed after 10-15 sec of contact. A similar construction utilizing the commercially available latex emulsion without DBS grafted to it was also tested for flammability. When the burner flame was removed after 10-15 sec, flaming of the substrate continued until extinguished about a minute later with water.

Latex Binder

A non-woven polyester fiber filter medium weighing about 1.25 oz/yd² was immersed in the 84.4/15.6-Airflex 4530/DBS graft latex. Upon drying at 300°F for 90 sec, the weight of the bonded fiber increased to 2.4 oz/yd². A second sample of non-woven polyester fiber filter was immersed in the commercially available latex (Airflex 4530) to which DBS had not been grafted. Upon drying, the bonded fiber weighed 2.3 oz/yd².

Both bonded fiber samples were tested for flammability by exposure to a four-inch high, 1950°F propane flame from a Fisher burner. The filter media were held 2-1/2 in. over the top of the burner at a 15°C angle from horizontal. The sample which was not bound with latex to which DBS was grafted burned the entire 12-in. length. The sample containing DBS graft latex burned between 8 and 9 in. prior to self-extinguishing.

Latex Sealant

Two latex sealants were prepared. The first was 95/3/2-EA/AN/AA latex prepared according to the procedure described in the Latex Sealant section of reference (33). The second was 80/20-the first latex/DBS graft latex prepared by the general procedure for synthesis of DBS graft commercial latexes.

To 100 parts of each of the two latexes mentioned previously were added 2 parts Triton X-405 (Union Carbide), 23 parts benzyl butyl phthalate, 4 parts Varsol #1 (Exxon), 2.5 parts ethylene glycol, 2 parts Composition T dispersant (Calgon), 120 parts calcium carbonate (2 micron average particle size), and 2.5 parts titanium dioxide. Both caulks showed good adhesion to substrates including wood, glass, and concrete by spot adhesion test (ASTM D 3808). In this test, a thin-bladed stainless steel spatula or probe is used to separate the caulk spot from the substrate.

The flammability of each was tested by placing a bead of caulk 1/4 in. in diameter on a 1/2 in. wide

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Table 5—Percent DBS Grafted onto Commercial Latexes

Example	Charge Ratio DBS/Latex	Latex Coagulated			Extract			Unextracted			
		wt, g	Br, %	PDBS, %	wt, g	Br, %	PDBS, g	wt, g	Br, %	DBS Grafted g	DBS Grafted[a] %
10	SBR latex 55 PDBS/45	2.004 1.100 PDBS	—	—	0.895	—	—	1.164	—	—	—
11	SBR latex blend + 0.900 SBR	—	—	—	1.383	43.62	1.062	0.673	<0.01	—	—
12	55 DBS/45 SBR	2.000	31.67	55.74	0.726	36.75	0.469	1.273	29.23	0.655	59.5
13	PB latex 60 PDBS/40 PB	2.003 1.200 PDBS	—	—	0.451	—	—	1.554	—	—	—
14	latex blend + 0.800 PB	—	—	—	1.447	39.90	1.016	0.624	<0.1	—	—
15	60 DBS/40 PB	2.000	34.34	60.44	1.117	34.35	0.707	0.893	22.85	0.359	29.9

(a) % DBS grafted = $\dfrac{\text{wt. of DBS grafted (unto commercial latex)} \times 100}{\text{wt. of DBS charged}}$

For example 12: $\dfrac{29.23 \times 100}{56.82} = 51.4\%$ — % of DBS grafted unto SBR latex in the unextracted portion.

1.273 g x 51.4% = 0.655 g — wt. of DBS grafted

$\dfrac{0.655 \times 100}{1.1} = 59.5\%$ — % DBS grafted

(DBS monomer used contains 56.82 wt.% bromine.)

strip of asbestos cement board. The caulk was subjected to the Butler chimney flammability test (ASTM D 3014). The first caulk, which did not contain DBS grafted to the latex, burned the full 250 mm of the test specimen. The caulk containing DBS burned less than 160 mm.

Latex Paint

Two latex paints were prepared. The first was 30/68/2-S/BA/MAA latex prepared according to the procedure described in the Latex Paint section of reference (33). The second was 80/20-the first latex/DBS graft latex prepared by the general procedure for synthesis of DBS graft commercial latexes.

In an open vessel with continuous high shear mixing, 40 parts by weight water, 0.15 parts antifoaming agents, dispersants and surfactants Tamol 731 (0.4 parts), Triton X-207 (0.28 parts), and Silwet L-7602 (0.28 parts) (Tamol is a product of Rohm and Haas, Triton and Silwet are products of Union Carbide), 0.62 parts sodium polyacrylate thickener, 18 parts titanium dioxide, 28.3 parts calcium carbonate, and 7.34 parts 1-butanol were added. Mixing speed was then reduced, and 50 parts latex was added. An additional 4.6 parts water, 1.15 parts methyl cellosolve, and 3 parts sodium polyacrylate thickener were then added. Composition A contained the first latex without DBS grafted on; composition B contained latex with DBS.

Paint compositions A and B had good adhesion to the Mylar film and film forming properties (ASTM D 3730). This test measures the resistance of removal of the coating from the Mylar film when scuffed or scraped. Each was used to coat a 1 mil Mylar film to a 10 mil wet thickness. The dry film measured about 3 mils. The dry film/Mylar was tested by the limiting oxygen index test (ASTM D 2863). Composition A without DBS had a limiting oxygen index of 22. Composition B with DBS had an oxygen index of 24, a significant improvement in flame retardancy.

DISCUSSION

This paper demonstrates that commercial latexes can be grafted with DBS monomer to produce FR latex products useful in a wide range of coating applications. Criteria include the T_g, physical properties, applications, and cost. One of the prime factors to be considered in the choice of a latex or a latex mixture to be grafted is the $T_g(s)$ of the polymer(s) in the final latex desired. Based on these criteria, we selected available commercial latexes, including acrylic latexes (Rhoplex HA-24 and HA-8, and Hystretch V-29 for binders, textile backcoatings, and adhesives), vinyl acetate-ethylene latex (Airflex 465 for adhesives), latexes of ethylene-vinyl chloride-third monomer which imparts amide functionality to the polymer (Airflex 4500, 4514, and 4530 for adhesives), SBR latex (Pliolite SBR for adhesive, foam, and rug), and butadiene rubber (BR) latex (PB latex for tires, retreads, and mechanical goods). We also synthesized acrylic latexes suitable for sealants and paints. Commercial latexes with T_gs greater than +29°C for modification were not chosen, because grafting of a high T_g (+141°C) PDBS onto commercial latexes will increase the T_gs of the final latexes. They will lose their original physical properties and become brittle, stiff, and not result in film formation upon coating.

As shown in *Table* 4, all the DBS-grafted commercial latexes (40-65% solids, 8.93 to 34.34% Br) passed the MVSS-302 flammability test with an SE rating. There is little difference between the observed T_gs of the commercial latexes and the observed T_gs of the DBS grafted latexes. We speculate that this could be attributed to the

short DBS grafted side chains. It is noteworthy that DBS grafted PB latex prepared by a redox system of potassium persulfate and sodium bisulfite passed the MVSS-302 flammability test (SE), whereas the graft latex prepared by a redox system of CHP and TEPA failed (RB, worst rating). This indicates that the former has a higher grafting efficiency than the latter as shown by the data in *Table* 5.

In order to understand the DBS grafting efficiency on the commercial latexes, we must select a solvent which dissolves ungrafted commercial polymers and homopolymerized DBS (PDBS) (ungrafted), but does not dissolve DBS grafted polymers. After the solvent extraction, the grafted portion is separated from the mixture of ungrafted portion. By analyzing the bromine contents in two separated portions in each sample, we can then calculate how much DBS has been grafted on the commercial latexes.

Two out of nine DBS-grafted commercial latexes, 55/45-DBS/Pliolite SBR (ex. 12, *Table* 5), and 60/40-DBS/PB latex (ex. 15, *Table* 5), were selected for THF solvent extraction to determine the percent DBS grafted (*Table* 5). The DBS homopolymer (PDBS) can be extracted by THF completely (ex. 11 and 14, *Table* 5). Thus, the unextracted PDBS residue could be considered to be grafted onto the commercial latex. The percent DBS grafted is given by the weight of grafted (or unextracted) PDBS divided by the weight of DBS charged. As shown in *Table* 5, ~ 60% DBS was grafted onto SBR and ~ 30% was grafted onto PB. These data may explain why DBS grafted SBR latex gave better flame retardant property than did DBS grafted PB latex.

Indeed, our results indicate that DBS can be readily grafted onto commercial latexes. However, % DBS grafted may depend on reaction conditions, initiators, and the composition of the latexes.

In our past experience,[34] FR efficiency of the DBS-based latexes is higher than that of a physical blend of FR DBS latex (PDBS) and a non-FR latex. In the present work, it was observed that FR efficiency of a DBS graft commercial latex is also higher than that of a physical blend. For example, at a comparable DBS content, both DBS grafted Rhoplex HA-24 and HA-8 latex coated 8 oz/yd^2 100% polyester fabrics at a weight of 1.4-1.6 oz/yd^2, passed the MVSS-302 flammability test with an SE (best rating) while a physical blend of ungrafted Rhoplex HA-24 or HA-8 latex with DBS homopolymers latex (PDBS) failed the test (RB, worst rating) (see Flame Retardance Testing and Results Section).

We plan to carry out research on solvent extraction of every DBS grafted latex other than DBS grafted SBR and BR latexes to determine DBS grafting efficiency. The structure of the various grafted polymers can be studied by electron microscopy, selective staining, cold stage, freeze fracture, and cryomicrotomy. Sometimes these techniques are not yet sufficienctly developed to yield a conclusive picture of the polymer structure. Spectroscopy (NMR, FTIR, ESCA) and chromatography (GC, GPC, HPLC, SEC, TLC, ITP, CHDF) continue to evolve in characterizing the graft latexes.

CONCLUSIONS

Dibromostyrene can be readily grafted onto nine commercial latexes plus two acrylic latexes via an emulsion polymerization technique. For example, THF solvent extraction of DBS grafted SBR and BR latexes yielded 60 and 30% DBS grafted, respectively. These data may explain why the former latex gave better flame retardancy than did the latter latex.

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All DBS grafted commercial latexes yield coatings with good flame retardancy without significant diminution of other physical properties. They are useful for a wide variety of applications in fabric backcoatings, contact adhesives, latex binders, latex sealants, and latex paints.

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Exhibit 4

REDACTED
IN ITS ENTIRETY